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R. H. Jones, D. R. Baer, C. F. Windisch Jr., R. B.  
Rebak

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## **CORROSION ENHANCED ENRICHMENT OF SULFUR AND IMPLICATIONS FOR ALLOY 22**

Russell H. Jones  
Exponent Failure Analysis Associates  
15375 SE 30th Place, Suite 250  
Bellevue, WA 98007

D.R. Baer and C.F. Windisch, Jr.  
Pacific Northwest National Laboratory  
P.O. Box 999  
Richland, WA 99352

Raúl B. Rebak  
Lawrence Livermore National Laboratory  
7000 East Ave, L-631  
Livermore, CA 94550-9698

### **ABSTRACT**

The uniform corrosion rate of Alloy 22 will define the lifetime of a component such as a waste container if all other degradation modes are not operative. This represents the best-case scenario because the experimentally determined uniform corrosion rates from multi-year tests is 0.01  $\mu\text{m}/\text{yr}$  or 0.1 mm in 10,000 years. This lifetime depends on the stability of the passive film over the lifetime of the container; however, this stability is unknown. One potential breakdown mechanism is corrosion-enhanced enrichment of sulfur to the surface leading to sulfur induced breakdown of the passive film. There are numerous studies that confirm that sulfur causes passive film breakdown in nickel based alloys and evidence exists for corrosion enhanced enrichment of sulfur in nickel and nickel alloys. However, neither sulfur enrichment nor sulfur induced breakdown of the passive film on Alloy 22 has been demonstrated. The results of preliminary studies suggest sulfur enrichment does occur at the alloy surface and that sulfur shifts the corrosion potential to more active potentials. No clear affect of sulfur was noted on the corrosion rate but the sulfur concentrations were about only 2–3 % of a monolayer, well below the concentrations that are possible.

Keywords: Alloy 22 (N06022), corrosion, sulfur-enhancement, surface-enrichment

## INTRODUCTION

The ultimate barrier protecting the nuclear waste from the environment in the Yucca Mountain repository will be a nanometer thick passive film. Even though the waste will be contained in a 20 mm thick vessel made from a highly corrosion resistant nickel alloy, this corrosion resistance is the result of a nanometer thick oxide film that forms in aqueous solutions. The lifetime of the container may then be defined by the uniform corrosion rate and the stability of the nanometer thick passive film. Therefore, mechanisms that could cause failure of the passive film during the long lifetime of the container are very important. There are mechanisms that are not measurable during standard laboratory test times, even long-term testing that may take years, that could cause film breakdown. One such mechanism is the enrichment of a species on the surface of the metal during extended periods and the breakdown of the passive behavior due to this enrichment. In this paper we first review chemical species that can cause a breakdown of the passive film over extended periods that would not be detectable during short laboratory test times then report on preliminary experimental results on corrosion enhancement of sulfur enrichment on the surface of Alloy 22 and the affects of sulfur on the corrosion behavior of Alloy 22.

Sulfur and phosphorus have been identified as two species that have the propensity to enrich at surfaces of metals and alloys and have been demonstrated to alter the stability of passive films on nickel and nickel base alloys. This enrichment could occur by the following processes: 1) thermal processing of the YM container, 2) long-term aging at repository temperatures resulting in surface segregation, 3) diffusion from the grain boundary or inclusions intersecting the surface, 4) adsorption from the environment and 5) enrichment during corrosion. Enrichment during thermal processing of the Alloy 22 container is detectable by standard laboratory tests since similar enrichment would occur during annealing of laboratory test samples. Segregation modeling has demonstrated that at repository relevant temperatures thermally activated enrichment does not reach significant concentrations within a 10,000 year time period so enrichment following emplacement is not likely. Diffusion from the grain boundaries and inclusions is also not likely since it depends on thermally activated processes and will be similarly limited by bulk diffusion. Therefore, adsorption from the environment and enrichment during corrosion are the two most likely processes to cause breakdown of the passive film over repository lifetimes.

Sulfur and phosphorus both enrich at interfaces and surfaces of metals and alter the corrosion behavior of nickel base alloys. But, there are many differences in the behavior of these two elements. Some of the reported differences include: 1) sulfur is more surface active than phosphorus so for a given bulk concentration it will be more highly enriched and once adsorbed to the surface it is more stable, 2) sulfur has been shown to enrich on the surface during corrosion of some nickel alloys while phosphorus has not, and 3) sulfur degrades passive film stability over a range of pH values while phosphorus can be detrimental at low phosphorus concentrations and low pH's but beneficial at high phosphorus concentrations over a wide pH range. Therefore, sulfur is considered the more potentially detrimental element for the long-term stability of the passive film on Alloy 22, although an experiment to determine whether phosphorus can enrich on the surface of Alloy 22 during corrosion is warranted.

There have been a number of studies that demonstrate the effect of surface adsorption of sulfur on passive film breakdown of metals. This adsorption has occurred from the environment, from biological processes and from enrichment due to corrosion. The studies showing surface enrichment during corrosion required concentrations of sulfur in the bulk material higher than the impurity concentration in order to accelerate the enrichment process. It was shown in studies where sulfur was enriched on the surface from the bulk and from the environment that the chemical state of sulfur is critical to its affect on passive film stability. Reduced forms of sulfur are more deleterious and oxidized forms less, or not,

deleterious. An oxidation state of +4 was sufficient to eliminate the affect of sulfur. Based on several analyses, it is possible for a critical concentration of sulfur (about 1 monolayer) to enrich on the surface of Alloy 22 in about 500 years at a corrosion rate of 0.01 micrometers/yr. Whether this enrichment will actually occur and whether it will cause a breakdown in the passive film cannot be determined from the existing database.

## **SUMMARY OF SULFUR EFFECTS ON CORROSION OF NICKEL BASED ALLOYS**

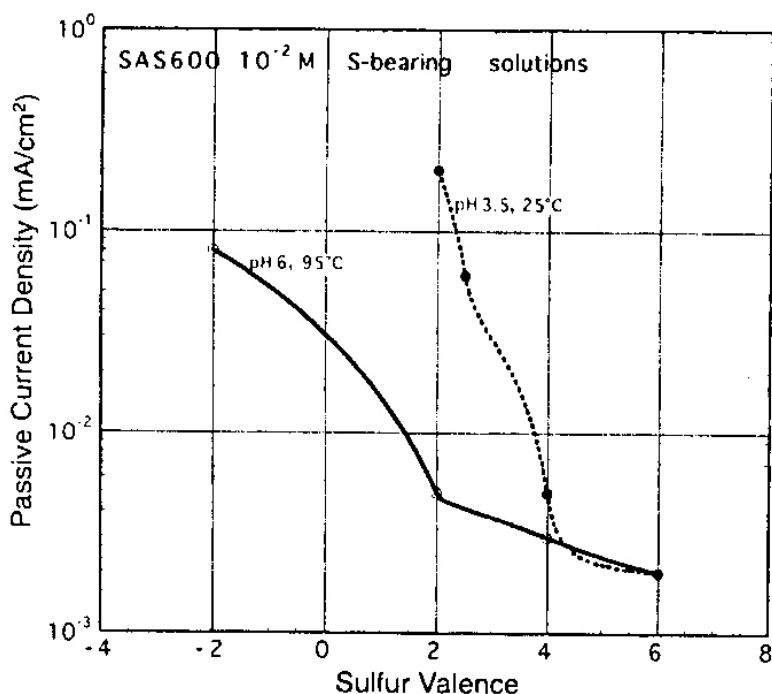
Numerous studies have demonstrated that sulfur degrades the corrosion performance of many metallic alloys especially alloys that rely on chromium for the formation of the passive film. One of the earliest observations of sulfur effects on corrosion was reported by Farrer and Wormwell<sup>1</sup> for iron in contact with a suspension of elemental sulfur in water. MacDonald et al.<sup>2</sup> confirmed the results of Farrer and Wormwell and showed that catastrophic corrosion of iron resulted after an incubation period that depended on the pH. Later studies on iron conducted by Okada et al.<sup>3</sup> reported on the effect of sulfur on the corrosion characteristics of iron used to contain carbonated beverages. They concluded that the adsorption of  $\text{SH}^-$  ions on the iron surface were responsible for the altered corrosion behavior of iron in these environments. Marcus et al.<sup>4-7</sup> reported on the effects of well controlled surface coverages of radioactive sulfur on nickel and Ni-Fe alloys. They demonstrated that a monolayer of sulfur was sufficient to increase the anodic current density and shift the active-passive transition to more noble potentials. The adsorbed sulfur was highly stable since it remained on the surface during dissolution and only began to decrease after anodic polarization to a potential of 600 mV (SHE). Marcus<sup>8</sup> summarized these studies in a recent review in which the mechanism for sulfur enhanced corrosion was proposed as the adsorbed sulfur causing a weakening of the metal-metal bonds that leads to a lowering of the activation barrier for dissolution of the metal atoms.

There is also evidence that adsorbed sulfur can alter the passive film on metals. Marcus et. al.<sup>4-7</sup> reported that one monolayer of sulfur shifted the active-passive transition of nickel to more noble potentials by about 100 mV. Marcus<sup>8</sup> concludes that the role of adsorbed sulfur on passive film growth is the blocking of surface sites for hydroxyl adsorption and hence passive film formation. Marcus<sup>8</sup> also noted that adsorbed sulfur retarded the passivation kinetics of nickel, Alloy 600 and copper. Below the critical adsorbed sulfur concentration of about 0.7 to 0.8 monolayer, a passive film will grow; however, the structure and properties of the film are modified by the presence of the adsorbed sulfur. Combrade et al.<sup>9-12</sup> also reported that sulfur, applied to the surface as radioactive sulfur, as done by Marcus et al.,<sup>4-7</sup> degraded the passive film on chromium containing alloys 600 and 690. The adsorbed sulfur led to increased intergranular corrosion and stress corrosion cracking. They proposed that sulfur supplied by either the environment or the material required an incubation period for the sulfur to reach a critical surface coverage.

Baer and Danielson<sup>13, 14</sup> and Windisch et al.<sup>15</sup> studied the effects of sulfur on the passivation of nickel and iron using a method where the sulfur is implanted into the surface of the metal sample. During corrosion the sulfur enriches on the surface and was found to alter the passivity of these metals. They reported the following for sulfur on nickel: 1) sulfur enriched to about 1 monolayer following corrosion, 2) that adsorbed sulfur was stable and remained on the surface of nickel during continued corrosion, 3) that the active-passive transition was shifted by several 100 mV in the noble direction by the presence of the sulfur, 4) that sulfur was strongly bound to the surface of nickel as determined by x-ray photoelectron spectroscopy, and 5) that polarization to high potentials oxidized the sulfur and eliminated its effect.

Iron showed some similarities and some differences to that observed for nickel.<sup>15</sup> Similar to nickel, there was a critical concentration of adsorbed sulfur to cause an increase in the corrosion rate but unlike nickel, the sulfur was not as stable and the current decreased with time over a period of seconds. Without sulfur the current decreased to very low values in ms, following a step in the potential to 750 mV (SCE). The iron studies were done in calcium nitrate which could be responsible for the differences.

Fang and Staehle<sup>16</sup> reported on the effect of the valence of sulfur on the passivation behavior of nickel alloys 600, 690, and 800. The valence was controlled in the solutions with sulfur in the forms of 1) sulfate, 2) sulfite, 3) tetrathionate, 4) thiosulfate, 5)  $S^{2-}$  and 6)  $HS^-$ . Fang and Staehle<sup>16</sup> showed very conclusively that the passive current density decreased substantially as the sulfur valence increased at a pH of 6 at 95°C and a pH of 3.5 at 25°C. The passive current density of Alloy 600 reached a minimum, of about  $10^{-3}$  mA/cm<sup>2</sup>, at a sulfur valence of +4 and a maximum, of about  $10^{-1}$  mA/cm<sup>2</sup>, at a sulfur valence of -2 for the pH 6, 95°C condition and +2 for the pH 3, 25°C condition, Figure 1. There were differences in the passive current densities for reduced sulfur but the minimum passive current density was achieved at +4 valence for both conditions. Baer and Danielson<sup>13, 14</sup> also noted that the valence of adsorbed sulfur altered its affect on the corrosion properties of nickel to that of active to passive corrosion. The current shifted from 200 mA/cm<sup>2</sup> to 0.2 mA/cm<sup>2</sup> with the oxidation of sulfur. The valence shifted from that for adsorbed sulfur, which is about 1 eV shifted from bulk sulfur, to that equivalent of the +4 valence of sulfate in solution observed by Fang and Staehle<sup>16</sup>. This shift corresponded to about a 5 eV shift in the energy that occurred as a result of polarizing to a voltage of +1 V (SCE) in the middle of the passive range for nickel in 0.5 N HNO<sub>3</sub>.



**FIGURE 1 – Passive current density versus sulfur valence for Alloy 600 in  $10^{-2}$ M solutions of sulfur oxyanions at pH=3.5 and 25°C and pH=6 at 95°C**

Besides affects on the anodic dissolution rate of metals and the stability of passive films, sulfur has been shown to increase the passive current density when present at levels below the critical concentration needed to destabilize the film. Oudar and Marcus<sup>5</sup> demonstrated by the use of reflection high-energy

electron diffraction (RHEED) that the structure of the passive film formed on nickel single crystals [Ni(111)] is different with subcritical concentrations ( $< 0.7$  monolayers) of sulfur present on the surface when the film forms relative to a clean surface with no sulfur. Without sulfur, a crystalline epitaxial film is formed while in the presence of sulfur the film is not epitaxial and a more defective polycrystalline film is formed. The corrosion rate of nickel is increased by a factor of four as a result of the sulfur induced defective passive film.

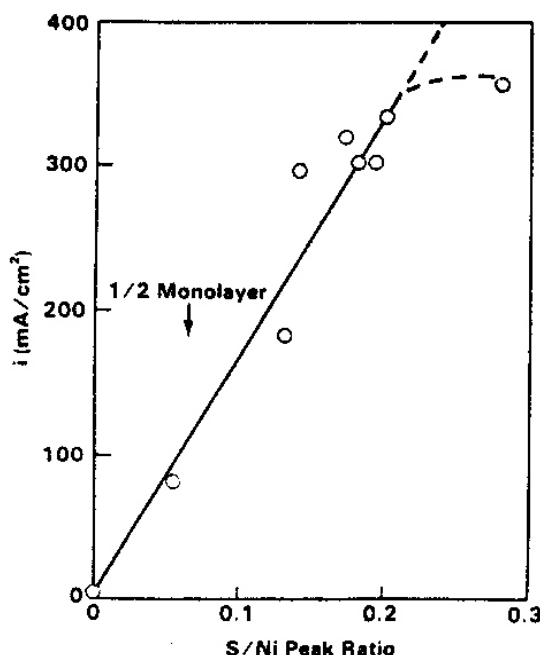
### **Processes that Concentrate Sulfur on the Surface and Evidence for Surface Enrichment**

Thermally Activated Processes. Sulfur is present as an impurity in most metals. In wrought nickel base alloys the chemical specification for sulfur is 150 ppm max. Lower concentrations are available in nickel base superalloys used for turbine blade applications but these are typically purified by triple arc remelting. Manganese or magnesium are added to nickel alloys to precipitate the sulfur as a compound to limit its effect on bulk properties. However, some will remain in solid solution within the nickel alloy lattice. Following thermal treatment some of the dissolved sulfur will be enriched at grain boundaries and other interfaces while the remainder will be randomly distributed throughout the metal. The dissolved sulfur is available to enrich on the surface of nickel alloys as a result of thermal treatments or anodic dissolution. Sulfur in the form of sulfides are not readily available to enrich the surface and affect general corrosion but they may contribute to localized corrosion at the point where they intersect the surface. Likewise, grain boundaries enriched in sulfur can be sites for localized corrosion. There is also some possibility for sulfur to diffuse from the grain boundaries onto the surface of metals. This phenomenon requires surface and grain boundary diffusion with grain boundary diffusion rates being rate controlling.

Impurities can also enrich on free surfaces of nickel-base alloys by thermal segregation as noted by Burton et al.<sup>17</sup> and anodic dissolution.<sup>5, 7, 12-14, 18-20</sup> Briant and Kuthra<sup>21</sup> also noted that segregation of sulfur to the interface between a surface oxide and the metal substrate in nickel-base alloys induced spallation of the oxide upon cooling to room temperature. The segregation occurred at 800 to 1100°C which are very high temperatures relative to that expected for the waste repository. Briant<sup>22</sup> however, has noted that surface segregation still occurs at much lower temperatures, even though the process is considerably more sluggish and complex than at higher temperatures. It is not obvious whether this process will occur in Alloy 22 at temperatures below 200°C and, if it does, whether it could be more severe than enrichment by anodic dissolution and breakdown of the passive film, mentioned above. Also, sulfur enriched on the surface during a high temperature annealing process must remain in a reduced form during subsequent handling to be detrimental to corrosion resistance which is very unlikely.

Corrosion Induced Enrichment. There have been a number of observations of surface enrichment of sulfur from the bulk material as a result of corrosion of nickel<sup>5, 7, 13, 14</sup>, Ni-25% Fe<sup>18</sup>, Ni-50% Fe<sup>19</sup>, iron<sup>15</sup> and Alloy 600<sup>20</sup>. Baer and Danielson<sup>13, 14</sup> studied this process using pure nickel samples and samples where sulfur was implanted in the near surface region to concentrations above the impurity concentration to accelerate the enrichment process. The surface sulfur concentration on nickel as a function of the S/Ni ratio is shown in Figure 2. The source of sulfur was impurity concentration of sulfur in the pure nickel samples. The increasing S/Ni ratio resulted from sulfur exposed and adhering on the surface during corrosion. The results by Marcus et al.<sup>5, 7, 18-20</sup> were produced by exposing the samples to an H<sub>2</sub>S-H<sub>2</sub> gas mixture at temperatures ranging from 1000 to 1200°C. This process enriched the surface similarly to the ion implantation process used by Baer and Danielson<sup>13, 14</sup> but to concentrations sufficient to form nickel sulfides during anodic dissolution. Marcus et al.'s<sup>5, 7</sup> results are shown in Figure 3. While Marcus et al.'s results are current versus polarization potential, the effect of

sulfur enriched on the surface during corrosion on the corrosion rate is clearly similar to those by Baer and Danielson<sup>13, 14</sup>. Baer and Danielson<sup>13, 14</sup> only observed monolayer coverage of sulfur on nickel. The impact of even small concentrations of sulfur in an alloy corroding very slowly over long periods of time could be significant. For instance, an alloy with 100 atomic parts per million (appm) of sulfur corroding at  $0.01 \mu\text{m/yr}$  will accumulate a monolayer of sulfur on the surface in 500 years if 100% of the sulfur atoms are retained at the surface. Baer and Danielson<sup>13, 14</sup> and Marcus et al.<sup>4-7</sup> found that a monolayer or less was sufficient to degrade the passive film of nickel.

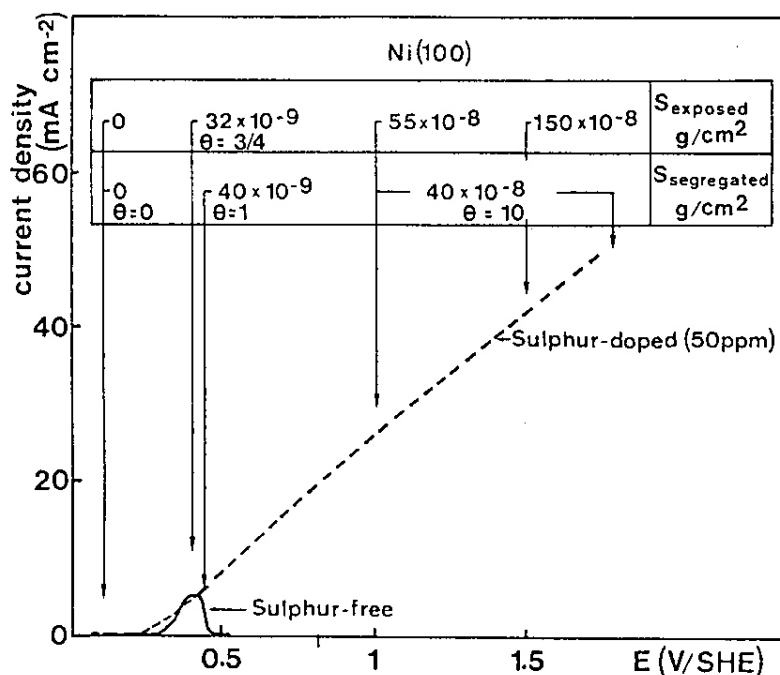


**FIGURE 2 – Steady state anodic current density at 0 mV [IR-free (SCE) on Ni in 0.5 N nitric acid at 25°C as a function of the amount of S on the surface**

Adsorption from the Environment. Sulfur species in the environment can adsorb on the surface and alter the corrosion behavior as noted by Fang and Staehle<sup>16</sup>. The sulfur ions in solution must adsorb on the surface to affect the corrosion rate. Marcus and Protopopoff<sup>23</sup> have treated the thermodynamics of the stability of adsorbed sulfur and oxygen on metal surfaces (iron, nickel, chromium and copper). They considered metals in water containing dissolved sulfur species such as S, H<sub>2</sub>S, HS<sup>-</sup>, HS<sub>2</sub>O<sub>3</sub><sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. They calculated E-pH diagrams (Pourbaix) that show the stability domain of adsorbed sulfur and these results showed that adsorbed sulfur is stable beyond that predicted for the stability of metal sulfides. Therefore, adsorbed sulfur can exist under conditions where bulk sulfide is unstable.

A third source of adsorbed sulfur is from the biological sulfur cycle as described in a review by Little et al.<sup>24</sup>. Metabolic by-products of the biological sulfur cycle can produce a range of reduced and oxidized states of sulfur including sulfides, bisulfides, hydrogen sulfide, thiosulfates, polythionates and sulfuric acid. Often these reactions occur directly on the metal surface to leave the sulfur or sulfur compound directly adsorbed to the metal. This method of accelerated corrosion is termed microbial influenced corrosion (MIC) and can occur over a wide surface area but is still more a form of localized corrosion than general corrosion.

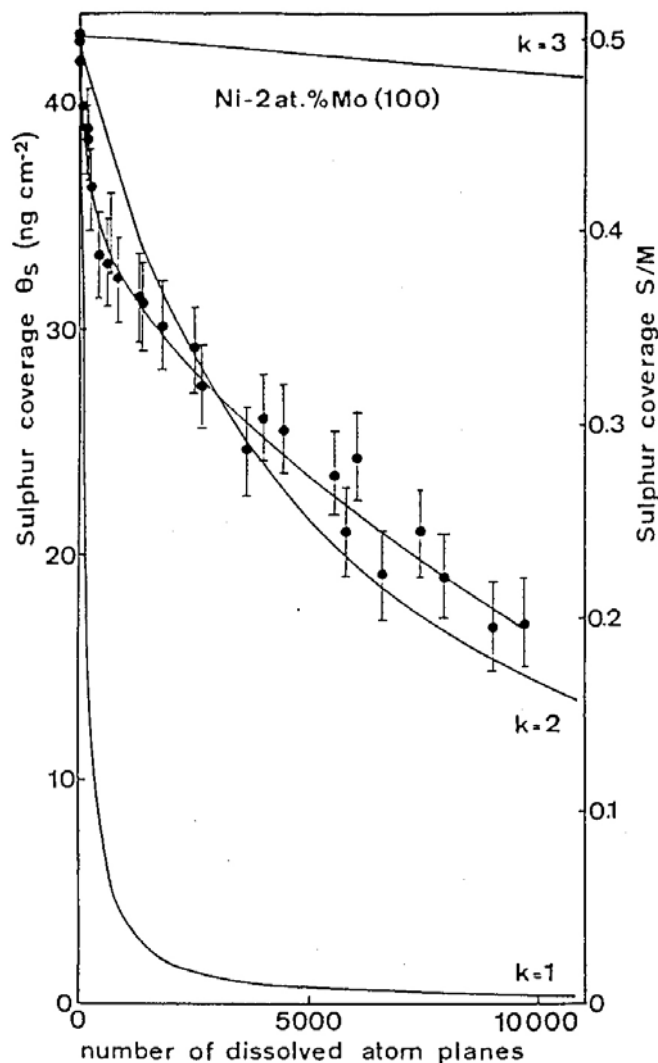




**FIGURE 3 – Surface enrichment of sulfur during anodic dissolution: *i*-*E* curves and radio-tracer measurements of the sulfur concentration on the surface of Ni(100) containing 50 ppm of sulfur (0.05 M H<sub>2</sub>SO<sub>4</sub>, 1 V h<sup>-1</sup>)**

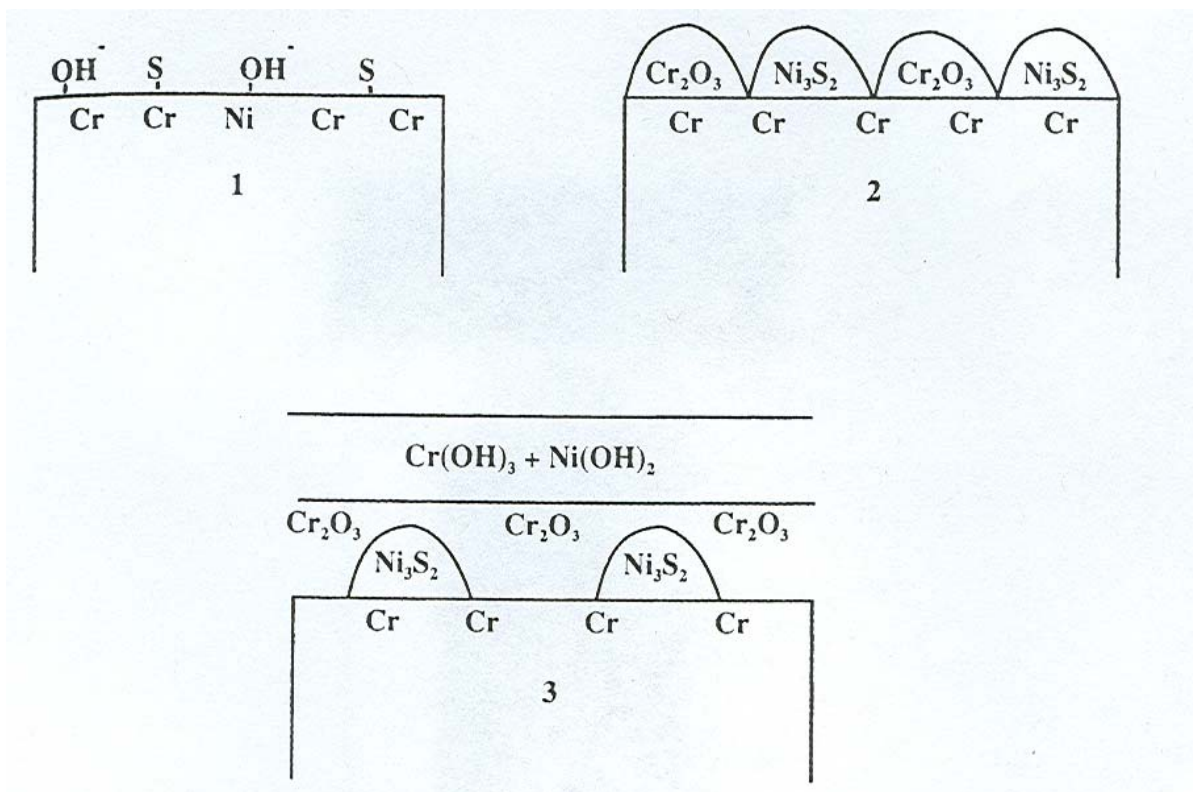
### Role of Alloying Elements in Anodic Sulfur Segregation Effects

There have been very few controlled experiments to determine the role of alloying elements in the adsorbed sulfur induced corrosion phenomenon. Most studies have been done on either pure metals or existing alloys. It is difficult to extract information on the role of elements such as chromium and molybdenum from alloy studies. Marcus<sup>25</sup> and Marcus and Moscatelli<sup>26</sup> evaluated Ni-2%Mo and Ni-6%Mo binary alloys to determine the effect of molybdenum as a single variable test. The tests were performed similarly to previous work where the samples were exposed to a mixture of H<sub>2</sub>S and H<sub>2</sub> to dope the surface with sulfur. The first difference noted relative to that for nickel was that the sulfur concentration decreased with corrosion instead of remaining constant, Figure 4. The sulfur loss is explained by a reaction between the molybdenum and sulfur to produce a compound that is readily dissolved. The reaction product was not determined but it was noted that the kinetics of sulfur loss could be explained by two molybdenum atoms per sulfur atom dissolving. That would be consistent with Mo<sub>2</sub>S. This is not a known compound so this ratio could result from a Mo-S-H<sub>2</sub>O complex that is readily dissolved. A similar molybdenum effect was also noted for Type 316 stainless steel that contains molybdenum<sup>27</sup>). Betts and Newman<sup>28</sup> evaluated the effect of tetrathionate on the corrosion properties of a range of stainless steel alloys modified to contain molybdenum concentrations ranging from 0.02 to 3.45 wt. %. They found the concentration of tetrathionate needed to activate corrosion increased with increasing molybdenum concentration. Betts and Newman concluded that the tetrathionate-molybdenum relationship was evidence for molybdenum reducing the sulfur surface concentration as observed by Marcus<sup>25,26</sup>.



**FIGURE 4 – The loss of surface sulfur induced by molybdenum (experimental and theoretical curves)**

The effect of sulfur enrichment on passivation of chromium containing alloys is not the same as that with molybdenum. This was shown by Marcus et al.<sup>12, 20, 29</sup> for nickel containing chromium in the range of 8 to 34 %. Unlike the effect of molybdenum, chromium does not cause a reduction in the adsorbed sulfur concentration but it promotes passivation in spite of the presence of adsorbed sulfur. X-ray photoelectron spectroscopy results confirmed the coexistence of nickel sulfide and chromium oxide. A schematic presented by Marcus<sup>8</sup> is given in Figure 5, showing the mechanism by which the nickel sulfide and chromium oxide could coexist and still result in a passivated surface. The presence of nickel sulfide on the surface occurs at higher concentrations of sulfur than needed for monolayer coverage and the presence of elemental sulfur. A question that the Marcus et al.<sup>12, 20, 29</sup> results don't answer is whether passivation will occur on a surface with a monolayer of elemental sulfur.



**FIGURE 5 – The mechanism of the antagonistic effects of chromium and sulfur on the corrosion resistance of Ni-Cr-Fe alloys**

## EXPERIMENTAL MEASUREMENT OF S EFFECTS ON THE CORROSION OF ALLOY 22

To explore the accumulation of sulfur on Alloy 22 during corrosion and the impacts of sulfur on corrosion processes, measurements have been conducted using Alloy 22 samples that have been implanted with sulfur. The first studies were to determine if the concentrations of sulfur achievable during the implant would alter the corrosion properties of the alloy. The next set of tests was oriented toward understanding the fate of sulfur exposed during surface corrosion.

### Experimental Procedure

Samples of Alloy 22, obtained from Haynes International (Kokomo, IN), had the following composition: 0.010 C, 0.29 Mn, 0.009 P, 0.001 S, 0.05 Si, 22.49 Cr, 12.58 Mo, 1.07 Co, 4.61 Fe, 0.19 V, 3.14 W, <0.01 Ti, Ni (remainder). These samples were cut into  $1 \text{ cm}^2$  (0.4 cm thick) square samples and then ground and polished to a 1-micron diamond finish. Some of these were then sent to Core Systems/Implant Sciences, Inc (Sunnyvale, CA) for implantation with S. Two implantation doses were chosen to achieve target peak compositions of 1 and 5 at. % S: 1) 50 keV and ion dose of  $3.0 \times 10^{15} \text{ ions/cm}^2$  to give expected S maximum of 1 at. % and 2) 50 keV and ion dose of  $1.6 \times 10^{16} \text{ ions/cm}^2$  to give an expected S maximum of 5 at. % based on calculated profiles. The peak maxima were expected at 20–25 nm under the sample surface. Ar ions were also implanted in other samples at a comparable dosage to give a similar concentration profile. The Ar-implanted samples were intended to serve as “control” samples that had no S, but a similar amount of implantation “damage.”

Electrochemical testing was performed using a PAR 273A potentiostat with PowerSuite software and a standard 3-electrode cell. The working electrode was the Alloy 22 specimen secured in a nylon sample holder that exposed 0.38 cm<sup>2</sup> surface area to solution. The counter electrode was a large-area Pt flag and the reference electrode was a saturated calomel electrode in a Luggin probe. Approximately 100 mL of solution was used for each test with the various compositions shown in Table 1, made up using reagent-grade chemicals and doubly-distilled water. All solutions were sparged with nitrogen and measurements were made under nitrogen in a glove box. For each electrochemical test, samples were equilibrated in solution for 1 h, while obtaining potential-vs.-time data. After 1 h, the polarization curves were obtained. Potential was scanned from 250 mV cathodic to the original open-circuit (corrosion) potential to 300 mV vs. SCE. The scan rate was 1 mV/s.

**TABLE 1**  
**pH BUFFERED SOLUTIONS USED IN THIS WORK**

pH Buffer	Measured pH	Composition
Unbuffered	-	1 M NaCl
KHP	3.67	1 M NaCl, 0.05 M Potassium Hydrogen Phthalate
Phosphate	6.36	1 M NaCl, 0.025 M KH <sub>2</sub> PO <sub>4</sub> , 0.025 M Na <sub>2</sub> HPO <sub>4</sub>
Borate	8.15	1 M NaCl, 0.0125 M Borax, 0.02 M HCl

The surface composition and oxidation state of the elements was measured using x-ray photoelectron spectroscopy (XPS) using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe with a focused monochromatic Al Ka X-ray (1486.7 eV) source for excitation, a spherical section analyzer, and a 16-element multichannel detection system. The X-ray beam was 105 W with a 100  $\mu$ m spot rastered over a 1.4 mm x 0.2 mm rectangle on the sample surface. The X-ray beam was incident normal to the sample and the X-ray photoelectron detector was at 45° off normal. Data were collected using a pass energy of 23.5 eV. For the Ag 3d<sub>5/2</sub> line, these conditions produced a full width at half maximum (FWHM) of 0.77 eV. The binding energy scale was calibrated using the Cu 2p<sub>3/2</sub> feature at 932.62  $\pm$  0.05 eV and Au 4f at 83.96  $\pm$  0.05 eV for known standards.

## Experimental Results

Effect of pH. Corrosion potentials and potentiodynamic polarization curves were measured for non-implanted samples of Alloy 22 in 1 M NaCl solutions containing the different pH buffers listed in Table 1. These measurements were used to define test conditions for more detailed study. Corrosion potentials were measured in two ways: 1) as the open-circuit potential observed after 1-h immersion in the test solution and 2) from the potentiodynamic curves. The corrosion potential values determined by these two ways differ for the reasons discussed below.

The corrosion potentials for the non-implanted samples measured after 1 hour equilibration in these tests are listed in Table 2 (along with results for the ion-implanted samples). The equilibration curves from which these values were obtained are given in Figure 6. The polarization curves for the same samples, initiated after the 1-h equilibration, are given in Figures 7 through 9 and the corrosion potentials determined from these curves are summarized in Table 3.

**TABLE 2**  
**CORROSION POTENTIALS MEASURED AFTER 1 H IMMERSION IN SOLUTION**

Solution	pH	Corrosion Potential after 1 h, V vs. SCE				
		No Implant or Sputtering	Implanted w/o Sputtering		Implanted and Sputtered	
			Ar	S	Ar	S
1 M NaCl (Unbuffered)		-0.260, -0.275		-0.330		
1 M NaCl + KHP Buffer	3.67	-0.210	-0.235, -0.235*	-0.245	-0.254	-0.270
1 M NaCl + Phosphate Buffer	6.36	-0.350				
1 M NaCl + Borate Butter	8.15	-0.270, -0.280*			-0.299	-0.312

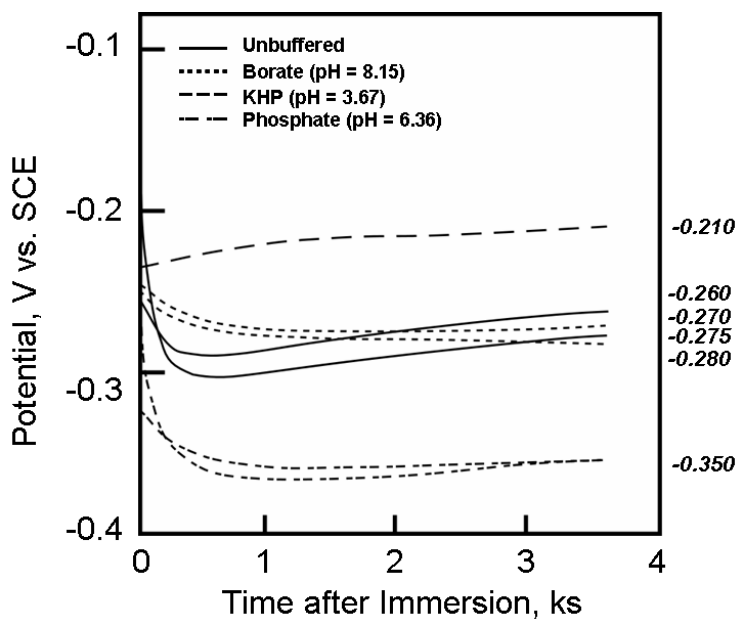
\*Duplicate run.

**TABLE 3**  
**CORROSION POTENTIALS FROM POLARIZATION CURVES**

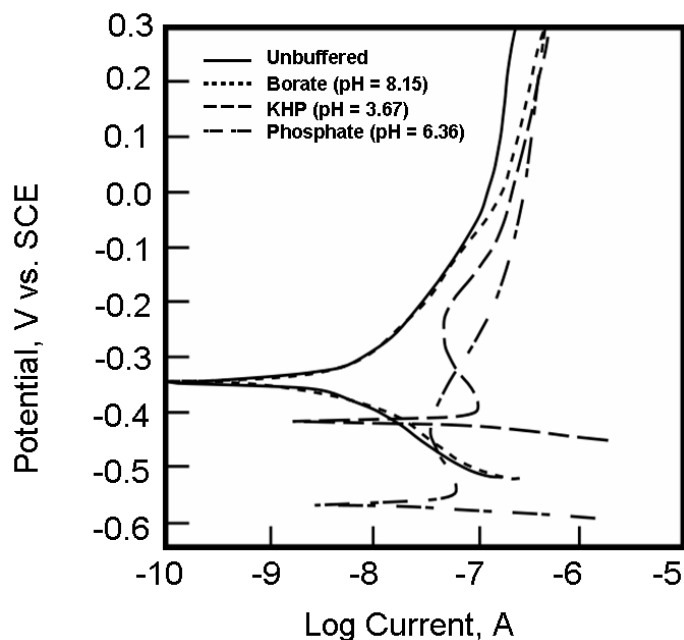
Solution	pH	Corrosion Potential from Polarization, V vs. SCE				
		No Implant or Sputtering	Implanted w/o Sputtering		Implanted and Sputtered	
			Ar	S	Ar	S
1 M NaCl (Unbuffered)		-0.347		-0.403		
1 M NaCl + KHP Buffer	3.67	-0.424	-0.365, -0.367*	-0.451	-0.402	-0.466, -0.449*
1 M NaCl + Phosphate Buffer	6.36	-0.575				
1 M NaCl + Borate Butter	8.15	-0.347			-0.349	-0.365

\*Duplicate run.

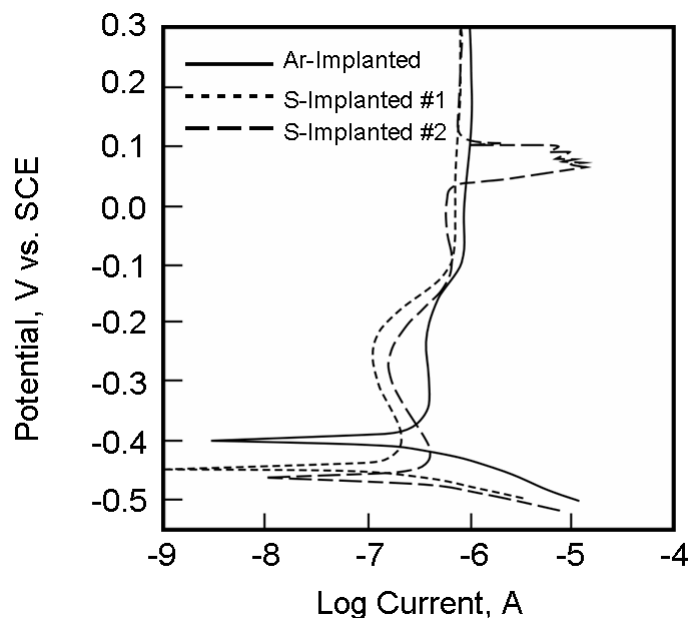
As shown in Tables 2 and 3, the corrosion potential was sensitive to the pH regardless of which approach was used. Values from the polarization curves are much more negative, however, and the trend is also different. For both approaches the values for the unbuffered and borate solutions are similar to each other. In both cases, the phosphate solutions gave the most negative values. The largest difference between the equilibration- and polarization-derived corrosion potentials was in the case of the KHP-buffered solutions, where the effect of polarization was to decrease the corrosion potential significantly relative to the other solutions.



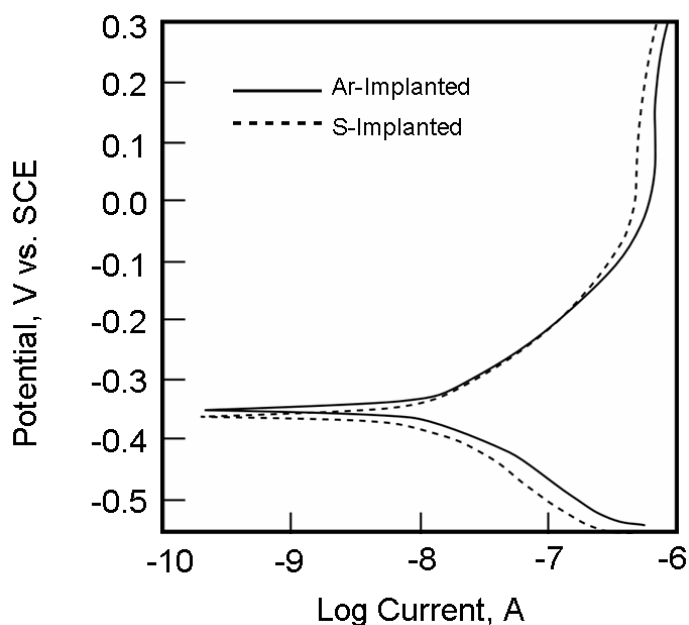
**FIGURE 6 – Corrosion potential vs. time for non-implanted Alloy 22 samples in deaerated 1 M NaCl solutions with different pH buffers. Samples do not have S or Ar in them. The corrosion potential after 1 h immersion is noted.**



**FIGURE 7 – Potentiodynamic polarization curves for Alloy 22 containing non-implanted elements in deaerated 1 M NaCl solutions with different pH buffers. Samples do not have S or Ar in them. Scan rate was 1 mV/s.**



**FIGURE 8 – Potentiodynamic polarization curves for Alloy 22, implanted with Ar and S (duplicate runs for S) and subsequently sputtered to the implant-concentration maximum, in deaerated 1 M NaCl solutions buffered to pH = 3.67 with KHP.**



**FIGURE 9 – Potentiodynamic polarization curves for Alloy 22, implanted with Ar and S and subsequently sputtered to the implant-concentration maximum, in deaerated 1 M NaCl solutions buffered to pH = 8.15 with borate.**

Sulfur Inventory and Chemistry. The electrochemical studies suggest only minor influences due to S on electrochemical measurements at the concentrations reported here. However, the accumulation and/or oxidation of S near the surface of the alloys could impact the nature of the corrosion. In particular the long term buildup of S might eventually alter the corrosion behavior as observed for Ni metal. In contrast, the oxidation of S could minimize any impact on corrosion as observed for Fe. The XPS measurements provide some information about both S build up and oxidation.

XPS data taken for S before and after exposure to solution or exposure to solution and polarization all show the S doublet to have a main photoelectron peak with a binding energy of 164.2 or slightly lower. Binding energies in this range are characteristic of elemental sulfur, a surface sulfide type layer and many metal sulfides. No peaks characteristic of oxidized sulfur were observed for any sample or any of the experimental conditions examined this study.

The lack of presence of oxidized S indicates either the non-oxidation of S in these studies or the removal of any oxidized S from the sample to the solution. The relative amplitude of the S photoelectron peak to those of the metal components provides an indication of S removal or buildup. Two different types of sample preparations were examined to test for S accumulation or removal. Corrosion tests were conducted on S implanted samples with and without sputtering. In particular, for the samples with no sputtering, the S to metal ratio ( $\text{at\%S}/(\text{at\%Ni}+\text{at\%Cr}+\text{at\%Mo})$ ) before and after the electrochemical tests were measured producing values of .019 and .032 respectively. If the possible impact of a carbon contamination layer is considered as described by Castle and Paker,<sup>30</sup> the corrected values are 0.017 and 0.028. This measurement suggests that the relative concentration of S to metals in the film was increased by about 70%. Although the intensity of the S signals are small, they are very reproducible. A second test involves looking at the S to metal ratio for a sample sputtered to the maximum S in the sample relative to the sample after the electrochemical test.. The last S signal collected during the sputter profile, provided a S to metal atomic ratio with little or no influence of O (from oxides present) or C (contamination). The S to metal ratio taken after the exposure of the sample to solution had both O and C influencing the data. We found that that initial S to metal ratio of the sputtered sample was 0.021 while the ratio after corrosion was 0.03 without the overlayer correction and .0206 versus .0254 with a correction. This also suggests some increase in the near surface S (25–45%) after the corrosion process.

Although these increases are small, they are consistently measured and the differences are outside the scatter in the data. In considering differences between these two measurements it may be useful to remember that we are looking at the ratio of S to sum of Ni+Cr+Mo. For the as received samples, the comparison involves S in the native oxide film that was involved in the implant process and S in the oxide film after corrosion exposure. The relative amounts of Ni/Cr/Mo are 17/16/3 before electrochemical treatment and 14/19/3 after the electrochemical treatments. Thus there appear to be only small changes in the film composition due to the electrochemical treatment. In contrast the samples sputtered to the S max, with most oxygen removed, had significantly different relative amounts of Ni/Cr/Mo (55/29/14) in comparison to (13/19/6) after the electrochemical treatment. As expected the solution exposure produces a Cr enriched oxide. The enrichment process may have some influence on the gain or loss of S over the short term.

It is interesting that the two S-implant samples tested in pH = 3.67, one of which showed a localized-corrosion-type excursion, also exhibited different corrosion potentials and that the more negative of these was for the sample that showed the current excursion. If the more negative corrosion potential reflects a very slightly higher S for this sample then it may be that the S concentrations studied in this work are on a threshold of a S-induced localized corrosion process. The possibility would be consistent with a similar threshold effect observed by our research group for S implanted into Fe-based alloys.



Following this line of reasoning, the sample that showed the current excursion could have had just enough additional S to lower the corrosion potential by the observed 10-20 mV and thereby exceed an activation threshold, coincidentally existent in this potential range, for a S-enhanced localized corrosion process. Further work needs to be performed in this area to test this hypothesis.

It is useful to compare these results to what might be expected. What follows is a simple estimation of the magnitude of enhancement in S signal that might be expected based on the corrosion that has taken place. The total charge that has passed through the sample during electrochemical treatment is approximately 0.00075 C. This corresponds very roughly to consumption of 0.7 nm thick layer of material. If we assume that none of the sulfur in the 0.7nm was removed and ask how much change in S signal would appear, we can use the exponential equation for XPS signals from Seah<sup>31</sup>. We first assume that no S is removed as 0.7nm of material is dissolved. Assuming that the alloy contained S at a 2% concentration initially and that the outer 0.7nm becomes enriched to 4% S during the electrochemical treatment (the S from the 0.7 nm of material dissolved remained in the outer 0.7 nm of material after electrochemical treatment) the ratio of corrosion enriched layer to the initial layer would be 1.25. Although there are many approximations in the calculation, the magnitude of the enrichment that would be expected is roughly the same as that observed. The XPS data suggest much of the S that appears at the alloy surface remains near the surface during corrosion of the alloy in the conditions examined in this work.

These S accumulation measurements imply that S does accumulate on the surface and provided motivation for an initial longer term measurement of S accumulation. One test of a sample in solution at open circuit conditions demonstrated that most if not all S remains on the surface during the open circuit corrosion and that the near surface concentration and accumulate to levels equivalent to several monolayers of S. The impacts of these larger S accumulations are yet to be examined.

## CONCLUSIONS

A review of the literature on the effects of sulfur on the corrosion behavior of nickel based alloys shows that sulfur can have a strong influence. This affect is most pronounced when sulfur is in the reduced chemical state and diminishes as sulfur is oxidized. Sulfur is very surface active and will adhere to metal surfaces especially nickel alloy surfaces. There is evidence that sulfur will enrich on the surfaces of nickel and some nickel alloys during corrosion but there are no reported results for Alloy 22.

The influence of S on the corrosion of Alloy 22 in deaerated 1 M NaCl solutions was examined using a combination of electrochemical and surface analysis methods. Results showed that at low surface concentrations there was a significant negative potential offset to the alloy (separate from the effects of ion implantation) and the effect appears to be related to the amount of S present. There was very little, if any, reproducible influence from the S when present in the surface layers of the alloy at concentrations up to about 2 at. % on polarization currents and morphology.

The presence of S at 2 at. % under conditions of this experiment *may* contribute to localized corrosion, however, due to the limited data reflecting this finding, future work needs to address this possibility further. This is especially true considering the small amount of corrosion obtained in these tests resulted still resulted in a measurable increase in the surface S concentration. Given a great amount of corrosion, over a longer period of time, it is important to determine if great S enrichment occurs (i.e. up to 100% or 1 monolayer) and what affect this might have on the corrosion performance of Alloy 22.

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